Detergents

Detergents

From the television screen, from the hoarding, from the pages of the magazine and newspaper, pours forth claim after claim: 'Washes Whiter', 'Adds Brightness to Whiteness', 'Contains Miracle X', and so on. Obviously we live in a world where detergents are important. But how does a detergent work? How does a washing powder take the grime out of a shirt or blouse? How does the grease disappear from the dinner plates when a few drops of liquid detergent are sprinkled into the washing-up water?

In order to understand the action of a detergent we must know something about surface chemistry. This is a special branch of chemistry dealing with the surfaces of materials. First of all, a word about soap. The word detergent comes from the Latin *tergere*, which means to clean. Soap is a detergent, the best known and certainly the oldest. For many centuries it was the only one.

Plant oils.
The palm tree, which grows in many tropical regions, is a valuable source of vegetable oil – for the manufacture both of edible fats and of soap. Here is shown a plantation of palms and palm kernels from which oil is extracted. The oil content of a kernel is about 50 per cent.
Unilever

Part One
Soap

Origin of soap – Soap originated, probably, in the ancient cultures that bordered the Mediterranean. There was natural soda in the Nile Valley, and also animal and vegetable fats. But we do not know how it was discovered that if soda and fat are heated together they produce soap. It is thought that the craft of soap-making was carried from Egypt to France by the Phoenicians in about 600 B.C., and it spread from there through Europe. Pliny, who died in the eruption of Vesuvius in A.D. 79, records that the best ingredients for making soap were goat's tallow and beech ashes.

Fats, as we have seen, provide one of the starting materials for making soap. Some fats, such as tallow or lard, come from animals, and others, such as coconut oil or olive oil, come from plants. But, whatever their origin, all fats consist very largely of a mixture of substances called 'glycerides'. These are chemical compounds made up of three units of fatty acid combined with one unit of glycerine. We can picture glyceride molecules as in this diagram.
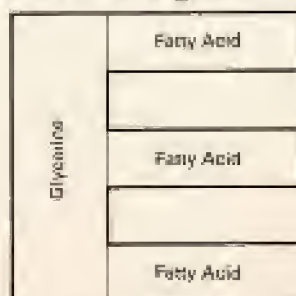
The other starting material for making soap is alkali – either potassium hydroxide (which is often derived from vegetable ash) or sodium hydroxide. When fat and alkali are heated, the al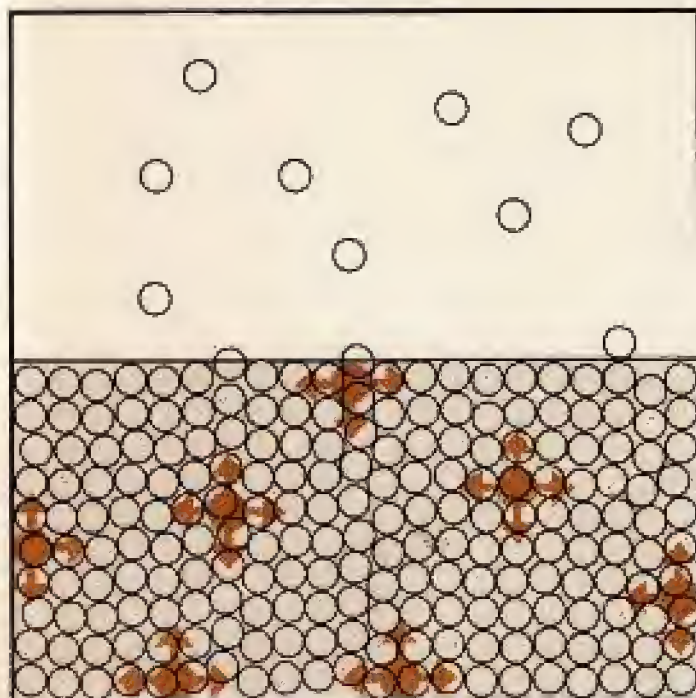kali breaks the glycerine-fatty acid bonds and combines with the fatty acids to form soap. (A diagram of a soap molecule is shown on page 5.)

Because alkali was in short supply soap remained scarce, and a luxury, for many centuries. Not enough was known about the chemistry of soap-making and without this knowledge there could be no systematic improvement in its manufacture. It was not until 1789, when a Frenchman, Leblanc, discovered how to make soda from common salt, and thirty years later, when another Frenchman, Chevreul, began to investigate oils and fats, that any real progress was made. From that period, matters began steadily to improve but two serious defects remained: the soap scum which forms in the wash is a nuisance; and fats are expensive.

It was not until the 1930s that chemists really began to investigate the mysteries of cleaning. They thought that they had discovered how soap removed dirt and they made several substitutes for soap but these were not particularly successful. Of the several properties that contribute to the washing power of soap, the chemists had discovered only one – the action by which soap helps water to *wet* clothes. Nevertheless this is a very important property; it is also one that needs some explaining.

If you drop some water on the back of your hand, you will notice that much of it runs off and what is left collects in droplets on the skin. Your hand is not evenly wet. If, instead, you drop some alcohol – or some kerosine – on your hand, you will see that the liquid spreads evenly over the skin. Alcohol and kerosine wet better than water. But, for a liquid to wash out dirt properly, whether from the body or from clothing, it must spread evenly over the surface that is being cleaned – in other words it must wet the surface. Why is it that water does not wet easily?

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The oddness of water – Water, one of the commonest of all substances, is also one of the strangest. If you look up your *Book of Data*, you will see that water has an unusually high latent heat of vaporization. This suggests that the molecules in liquid water are held together by very strong intermolecular forces.

Beneath the surface of the water, each molecule is attracted from every side (as shown in the diagram), but molecules at the surface can experience no attractions from above. (The surface of a volume of water includes not only that between the air and water but also the interface between the sides and bottom of the container in which the water is held and of any object submerged beneath the water.) Because there is no attraction from above, water molecules at the surface will be attracted inwards by the molecules below and it is this attraction which accounts for the fact that water does not 'wet' easily. It is almost as if there were a 'skin' on the water surface. Water molecules on, for example, the surface of a fabric are attracted to each other more strongly than they are to the fabric molecules. The water will not wet the fabric properly. On a waterproof fabric or on your hand, the attraction is almost zero. To increase the wetting power of water, something must be introduced to loosen the 'skin' on the water surface. This brings us back to soap.

How soap works – We have seen how soap is made from fat and alkali but, to understand how soap washes, we must look more closely at its structure. It is the fatty acids, which are combined with glycerine in the fat, which interest us. Soaps are characterized by a long hydrocarbon chain, as shown in the diagram opposite.

For simplicity, we shall denote this chain by R. At the end of the chain there is an organic acid group (-COOH). Thus, the general formula for a fatty acid is: R — COOH.

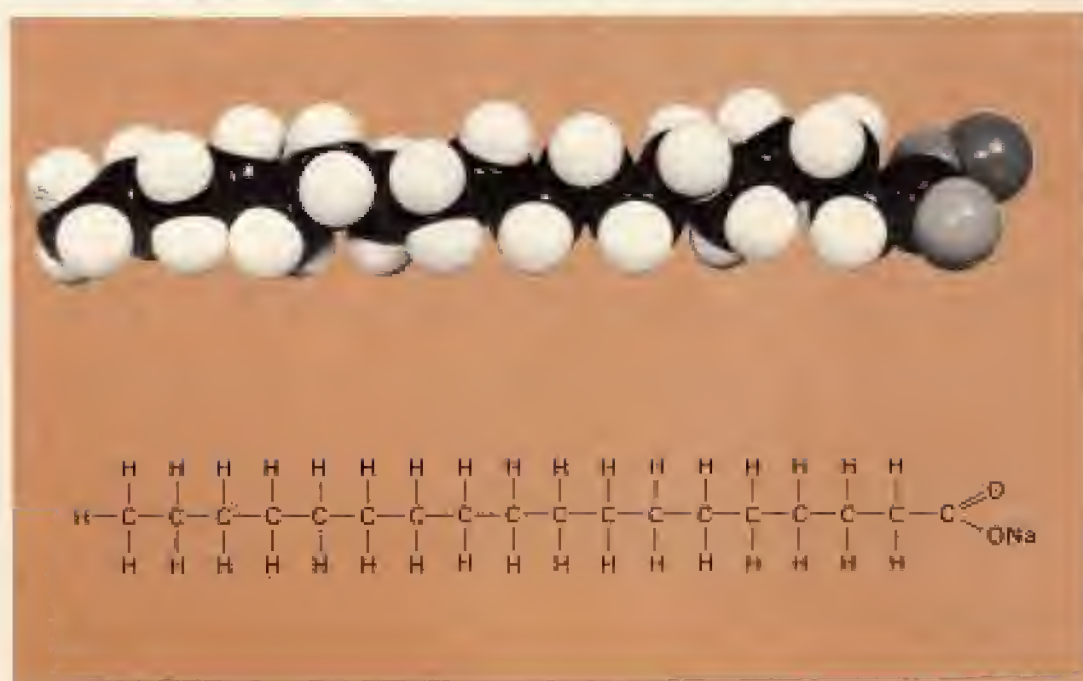The fatty acids which occur most commonly in fats are: palmitic acid, the formula for which is $CH_3 (CH_2)_{14} COOH$; stearic acid, $CH_3(CH_2)_{16}COOH$; and oleic acid, $CH_3 (CH_2)_7 CH=CH (CH_2)_7 COOH$.

There is also lauric acid, $CH_3 (CH_2)_{10} COOH$, which is the

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Measuring the pull on the surface of a liquid – with a thin glass plate held horizontally on the liquid surface.
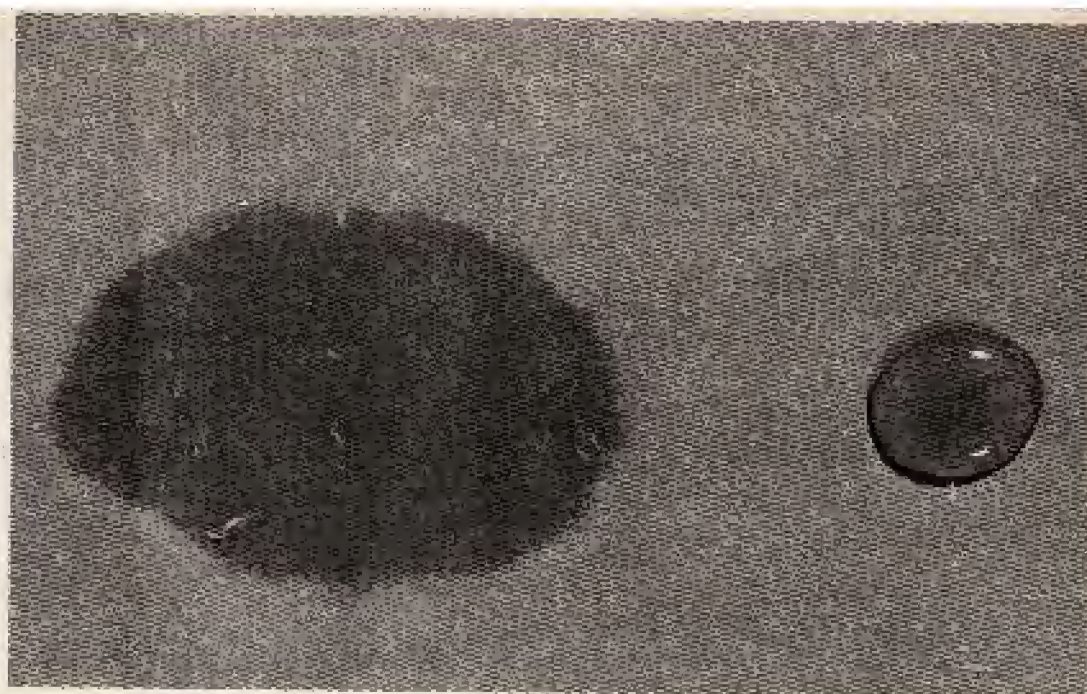*Shell*

Molecular model of a typical soap—sodium stearate ($C_{17}H_{35}COONa$).

main fatty acid in coconut oil and palm-kernel oil. Lauric
acid is an important constituent of toilet soaps because it im-
proves their texture and lather.

To make soap, the fatty acids are made to react with
potassium hydroxide or with sodium hydroxide, as follows:

$$R - COOH + NaOH \rightarrow R - COONa + H_2O$$

fatty   sodium   soap
acid   hydroxide
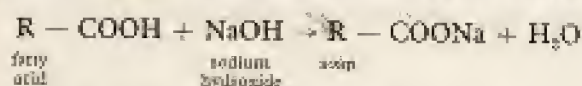
In solution in water, the soap ions, $RCOO^-$ and Na^+,
separate from one another.

The hydrocarbon chain has no charge on it, and is by far
the larger part of the soap ion. The water molecules, which
attract the negatively charged acidic groups as well as each
other, try to squeeze the hydrocarbon chains out of the way,
and we can imagine any one soap ion as being anchored at
one end and continually pushed about at the other. On the
surface of the water, the hydrocarbon chains are pushed right
out, although the soap ions are still anchored to the water by
their acidic groups. The whole water surface becomes cov-
ered with soap ions, their chains projecting vertically out and
their acidic heads anchoring them below, thus:

We call such a covering a monomolecular layer. You may
remember that, by measuring the volume of an oil drop and
the area of the monomolecular layer which it formed, we
were able to calculate the size of the oil molecules.

There is little attraction between the hydrocarbon 'ends'
of the soap ions, and therefore the covering of the water sur-
face with these ions has the effect of loosening the 'skin' of
the water. As a result, the soap solution flows over a surface
(for example, a fabric) and wets it more readily than plain
water would do. We see that the essential features of the mole-
cule of a wetting agent are a water-attracting (hydrophilic)
head, and a water-hating (hydrophobic) tail. How wetting
helps the washing process is described in the next part.

Synthetic detergents

The first non-soapy detergent – Even before the wetting action of soap was understood, someone had made the first non-soapy detergent. In 1834 Edmond Frémy, a Frenchman, heated olive oil with sulphuric acid, poured the concoction into water, and neutralized it with alkali. As far as we know he did this solely out of curiosity and without any intention of making a substance with soaplike properties. However, he found that the stuff he had made foamed and cleaned greasy objects and so behaved like soap.

The glyceride molecules that make up olive oil contain a high proportion of oleic acid, a fatty acid we have already mentioned. What had happened in Frémy's experiment – although he did not know it – was that the sulphuric acid had reacted with the oleic acid groups in the glyceride molecules to produce a sulphated oil. When poured into water and neutralized with sodium hydroxide, the oil had yielded sulphate ions attached to a hydrocarbon tail. The structure looks something like this:

Here, as you can see, the hydrocarbon tail is much more complex than the one in the soap molecule.

An important difference between sulphated oils and soap is the way they behave in hard water. We say water is hard when it contains a high proportion of dissolved calcium and magnesium salts. This happens when the water originates in chalk or limestone areas. Calcium and magnesium ions react with soap ions to form soaps which, unlike those of sodium and potassium, are insoluble in water and which clump to-

gether to produce scum. Scum not only wastes the washing power of soap, it also sticks to clothes. If the washing water contains a sulphated oil, the calcium and magnesium ions form soluble substances. There is no scum and nothing to stick to the clothes.

Wetting agents – Sulphated oils were not an ideal alternative to soap, although they proved useful in the wool-scouring trade. Also, like soap, they were made from expensive fats, so chemists looked for other wetting agents. Once the structure of a wetting agent was understood, there were many approaches. All of them involved the making of substances which had a molecule with a hydrophilic head and a hydrophobic tail – and this making of new substances is something at which chemists of the past fifty years have shown themselves to be very adept. In practice it was (and still is) important to take into account the availability and cost of raw materials.

At present there is a great variety of wetting agents. In this Background Book, we confine ourselves to the two most common types: those which ionize in solution (as soap does) and are called 'anionics'; and those which do not ionize and are therefore known as 'nonionics'. About 95 per cent of washing powders and washing-up liquids are made from anionics. Anionics foam more readily than nonionics and people tend to associate foam with good washing. In fact, foam is necessary for toilet soap, where it makes a concentrated solution for application to the skin, and for shampoos where the solution has to stay put while it is worked into a mass of hair. But in a domestic wash the clothes are agitated below the surface and foam does nothing to help – except to indicate that active detergent is still present in the solution.

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*Anionics* – The cheapest raw material from which non-soapy anionic detergents are made is propylene ($CH_2 - CH = CH_2$) – a gas that is usually derived from petroleum. Propylene molecules can be made to link together to form a longer hydrocarbon chain. The linking of molecules to form chains – called a polymerization reaction – is more fully described in the Background Book *Plastics*. The chain is not straight like that of soap but is what we call a branched chain (see upper diagram on the opposite page). Usually it contains about twelve carbon atoms.

The branching does not affect the wetting power of the detergent but it has an unwanted side effect – foam that is difficult to get rid of. Most waste water passes through drains to sewers, then to rivers, and finally to the sea. On this journey any solid or dissolved matter in the water is subjected to attack by bacteria. Soap is broken down by bacteria. But bacteria cannot digest branched-chain hydrocarbons, and this explains why we see foam on many rivers today. Chemists are solving this problem by producing hydrocarbons with straight chains which bacteria can digest.

The branched hydrocarbon is not itself a wetting agent. By

itself it would simply form an oily layer. Each molecule lacks a hydrophilic head. This hydrophilic head is introduced into the hydrocarbon structure to hold it in the water in the following way: the hydrocarbon is combined with benzene to give alkylbenzene. Benzene, although it does not add to the wetting properties of the detergent, combines readily with sulphuric acid (or sulphur trioxide) to give alkylbenzene sulphonic acid; finally, the sulphonic acid is neutralized with sodium hydroxide to give sodium alkylbenzene sulphonate. We can summarize the manufacturing steps as follows:

$$R\langle\bigcirc\rangle \xrightarrow[(SO_3)]{sulphur\ trioxide} R\langle\bigcirc\rangle SO_3H \xrightarrow{sodium\ hydroxide} R\langle\bigcirc\rangle SO_3Na$$

alkylbenzene   alkylbenzene   sodium alkylbenzene
                      sulphonic acid   sulphonate
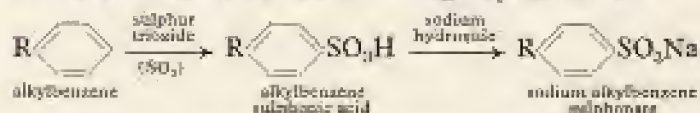
You will notice that this product is called a sulphonate, whereas the treated olive oil was called a sulphate. The difference is that, in a sulphate, we have the group – OSO_3Na, and, in a sulphonate, the group – SO_3Na, but the hydrophilic property is similar. In solution, the sulphonate ions separate:
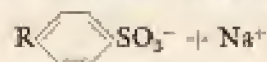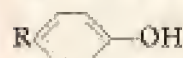
$$R\langle\bigcirc\rangle SO_3^- + Na^+$$

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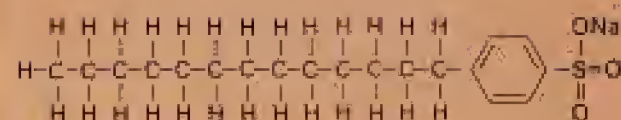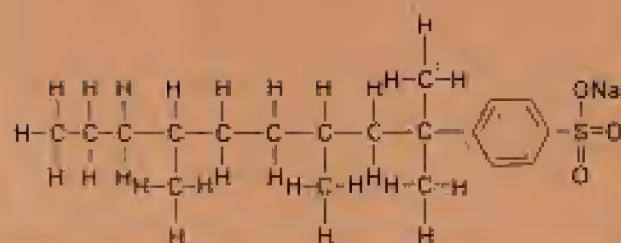
The $(-SO_3^-)$ forms the water-soluble hydrophilic head of the wetting agent, and $\left(R\!\!-\!\!\bigcirc\!\!-\right)$ forms the water-insoluble hydrophobic tail.

Nonionics – In the manufacture of nonionics, the starting material is not alkylbenzene, but is usually alkyl phenol.

$$R\!\!-\!\!\bigcirc\!\!-\!\!OH$$

This is treated with ethylene oxide (CH_2CH_2O).

The ethylene oxide molecules open out to form a chain which links on to the phenol, thus:

$$R\!\!-\!\!\bigcirc\!\!-\!\!OH \quad CH_2\!-\!CH_2 \quad CH_2\!-\!CH_2 \quad CH_2\!-\!CH_2 \ldots$$

$$R\!\!-\!\!\bigcirc\!\!-\!\!OCH_2CH_2OCH_2CH_2 \ldots \ldots OCH_2CH_2OH \text{ or}$$
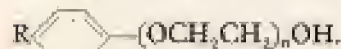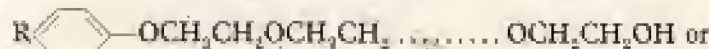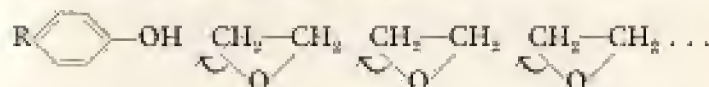
$$R\!\!-\!\!\bigcirc\!\!-\!\!(OCH_2CH_2)_nOH.$$

Here $(OCH_2CH_2)_nOH$ constitutes the water-soluble head and, again, $R\!\!-\!\!\bigcirc$ the water-insoluble tail. Since the lengths of both R and $(OCH_2CH_2)_nOH$ can be controlled in production, so the water-soluble/insoluble balance between the two ends of the molecules can be modified according to requirement. Nonionics are used in such specialized operations as the cleaning of metal surfaces.

The two types of detergent that we have described – anionics and nonionics – by no means exhaust the list. Chemists have devised a bewildering assortment of wetting agents, with marked differences in behaviour. New requirements and new raw materials present new problems to be solved.

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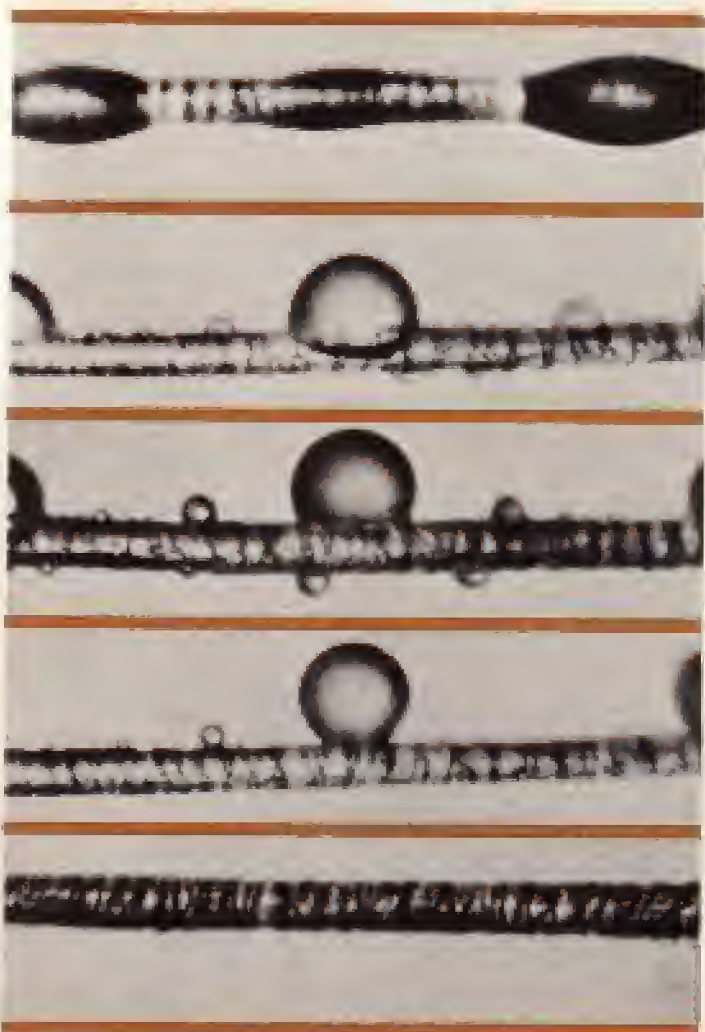
The way in which a detergent removes grease from a fibre. The hydrophobic tails of the detergent molecules are attracted by the grease and the hydrophilic heads are attracted by water. Water penetrates between the grease and the fibre, and the grease rolls up into a globule and becomes detached —as shown in the diagram (above) and the series of photographs (left). The grease globules are kept dispersed by their coating of detergent ions.
*Photograph, British Launderers' Research Association; diagram, Unilever*

Getting rid of clay – A wetting agent cannot, by itself, remove all dirt from fabrics. We can broadly characterize dirt as greasy and non-greasy (or particulate). A wetting agent will remove grease from a fabric, but particulate dirt is always present. This consists mainly of clay particles, but there is usually soot and rust present as well. The clay is the trouble-maker. Clay, which is a compound of calcium and silicon, forms tiny platelets; these platelets adhere strongly to fabric. Soap ions have the power of drawing calcium ions out of clay, and this loosens the grip of the clay on the fabric. The calcium ions then combine with the soap to form scum – which joins the scum already formed from the hardness of the water.

Non-soapy wetting agents do not have this power of draw-ing calcium out of clay. Therefore they must incorporate a substance which does – usually sodium phosphate. The nega-tively-charged phosphate ion is able to pluck, as it were, a positively-charged calcium ion from a clay molecule. To-gether the two ions form a complex ion which is soluble. It stays in solution and does not form a scum.

How dirt is removed – Let us now consider just how dirt is removed. Everything in contact with a detergent solution, be it fabric, grease, or dirt particle, creates a surface in the solution, and detergent molecules are pushed out at the surface with their hydrophobic tails protruding. Thus the fabric and dirt become covered with a monolayer of detergent molecules, with their hydrophilic heads on the outside in the water.

The layer of detergent molecules overlying grease on fabric causes both the grease and the fabric to attract water molecules. In other words, the detergent has increased the wetting power of the water. The water penetrates between the grease and the fabric; the grease rolls up and becomes detached; and finally the grease forms an emulsion with the water. In an emulsion two substances which are insoluble in each other (in this case, grease and water) are induced to come together by introducing a third substance (the detergent) which has an affinity for both the others.
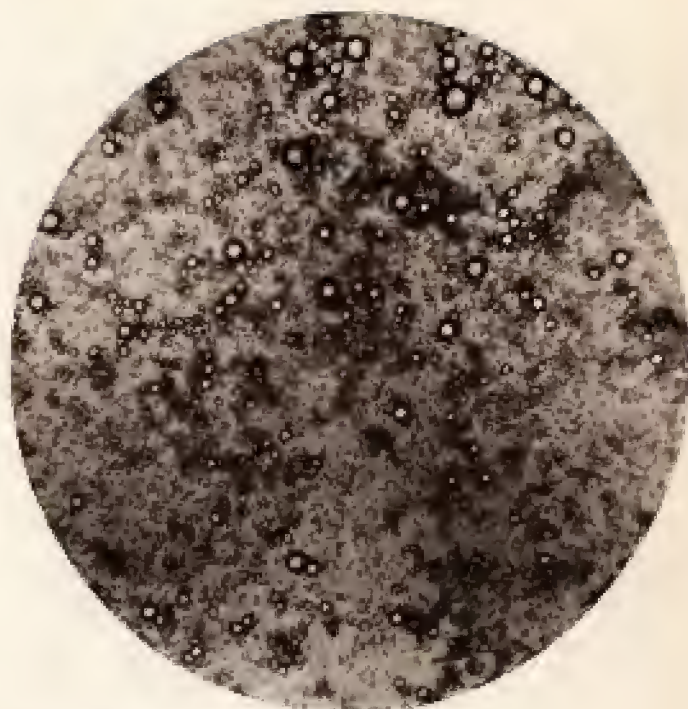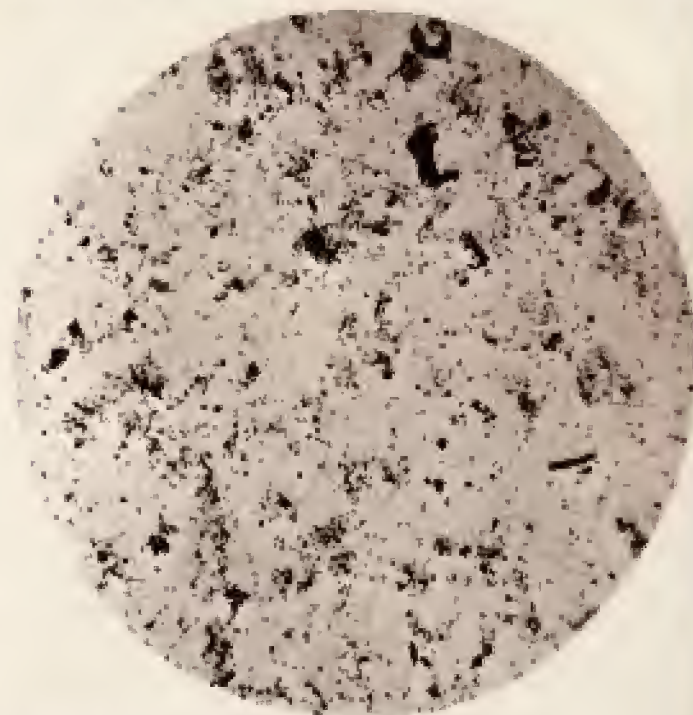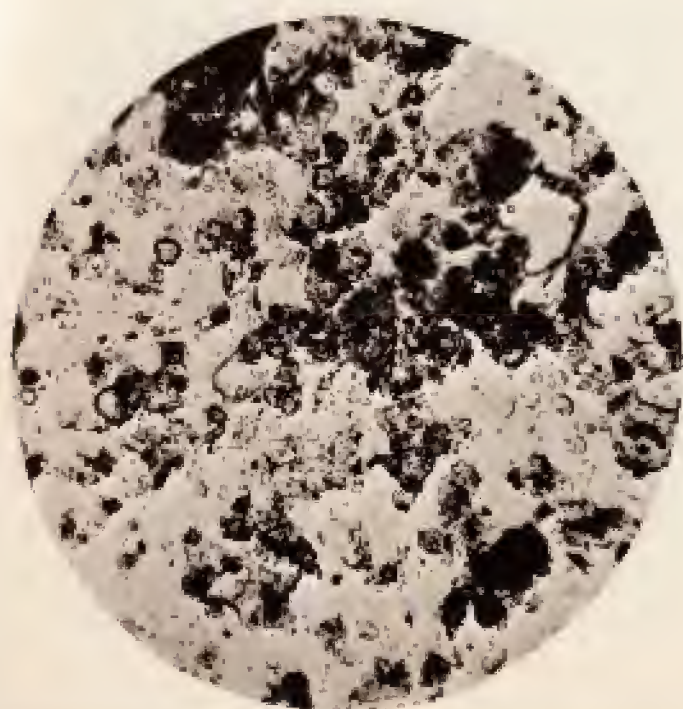
Grease dispersion. Photo-micrographs of grease dispersed in a soapy solution. In the right-hand picture, the grease has been broken down into very small globules.
*Unilever*

Dirt particles (including clay, after the calcium has been got rid of) are removed in the same way, but here, because one of the substances is an insoluble solid, a suspension and not an emulsion is formed. Agitation – as in a washing machine – is required finally to detach the dirt. The negative charge on the particles, stemming from their coat of detergent ions, tends to disperse them and keep them dispersed; but the charge is not strong enough to prevent some of the dirt from being attracted back to the fabric. To discourage this, a small quantity of a dirt-suspending agent is put into the product. This increases the charge on the particles and keeps the dirt dispersed more effectively.

Stain removal – Discoloration through staining is another problem. Water-soluble stains go back into solution and are easily removed. Others must be bleached chemically. Bleaching is a simple matter of oxidation, but the oxidizing substance must not damage the fabric in removing the stain.

Fabrics may be stained by accident, but there is also a tendency for them to yellow with age. Till quite recently, this was countered by use of the 'blue bag', a package of slightly soluble blue dye which, by adsorption on the fabric, counteracted the yellowness. Today, this is done more effectively with fluorescent dyes, which absorb light of one wavelength (generally ultra-violet) and rediffuse it as light of another. Because the dyes chosen remit blue light, the yellowness in the fabric is counteracted.

Dirt dispersion. Photomicrographs showing:
a clumps of greasy dirt in plain water.
b dirt broken down and dispersed in a soapy solution.
Unilever
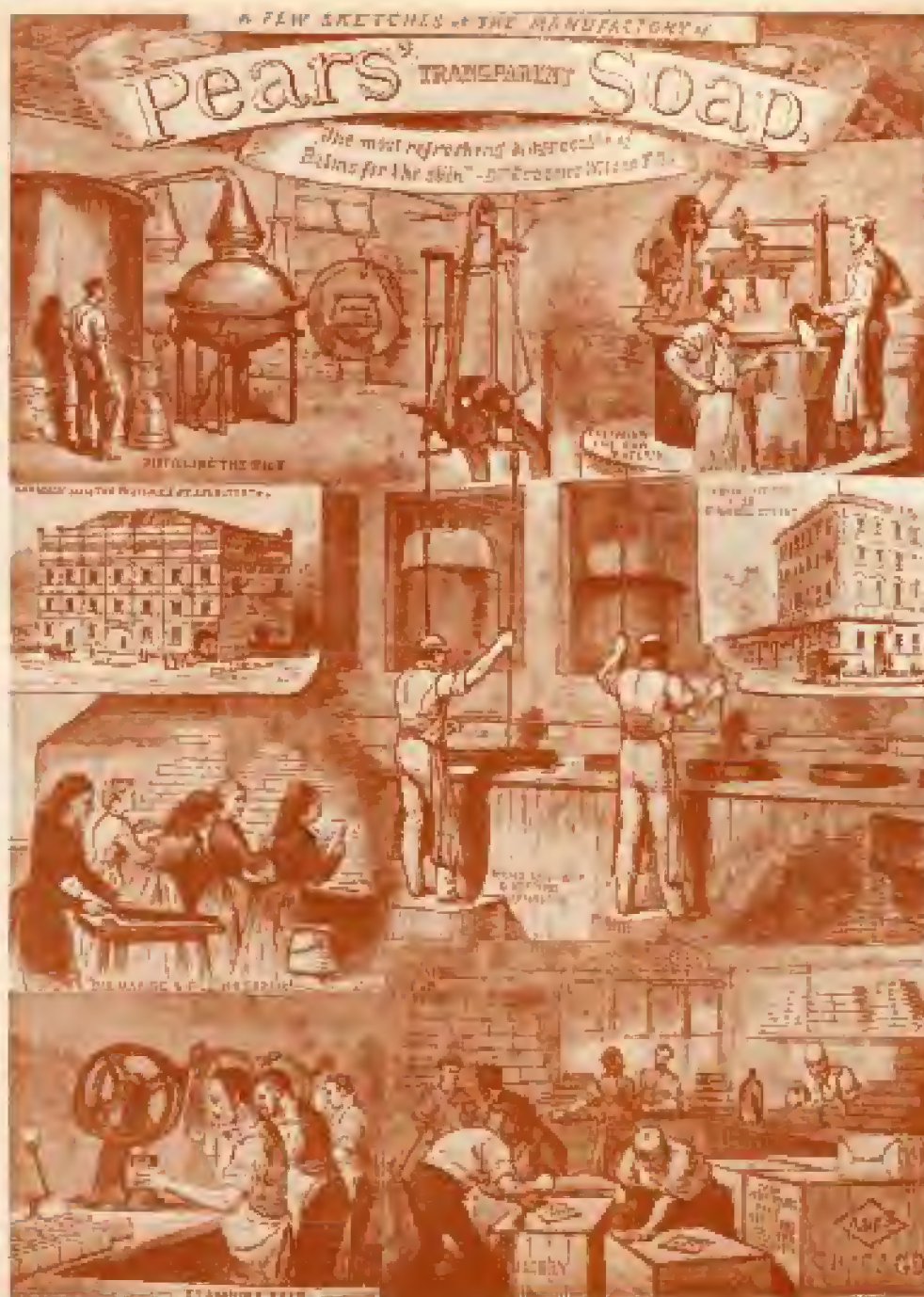
This page from *The Illustrated London News* of 1878 depicts the 'batch' manufacture of a well-known brand of soap. Processes shown include: distillation of oils; preparation of raw materials; mixing machines; box-making; soap-stamping; and packing for export.
Unilever

Manufacturing detergents

Making soap and soap-powder – The way soap is made has remained the same for many years. But whereas formerly it was made in batches – that is, successive lots of fats were saponified (reacted with sodium hydroxide), refined, cooled, cut, and stamped – now the process is continuous. It is like a conveyor belt and a continuous process of this kind presents a number of technical problems for chemical engineers to solve. Fat and sodium hydroxide are fed together into a saponifying vessel in which they react. Afterwards the reaction mixture is fed through another vessel where the glycerine, freed during saponification, is washed out with brine.

If the soap is to be made into tablets, it is sprayed hot into a vacuum chamber. The particles of soap dry and cool by evaporation as they fall into the chamber. They are scraped from the walls and pass to a refining vessel. There they are scented and the soap is worked between heavy metal rollers to impart texture. Through a metal die, the soap is ejected from the refining vessel in the form of a continuous bar which is cut into billets. The billets pass through a cooling tunnel to a stamping and wrapping machine.

Other factors, apart from its ability to wash, have to be

In soap manufacture, after the glycerine freed during saponification has been washed out with brine, the soap is boiled with a little water to remove impurities (as shown). When left to settle, a layer of 'neat' (70 per cent) soap forms at the surface and this is skimmed off for processing into tablets or powders.
Unilever

Manufacturing a non-soapy detergent powder. This is the top of the drying tower where a hot mixture of the ingredients is sprayed in. As the droplets of the mixture descend, they meet an upward current of hot air; water in the droplets evaporates, and the droplets expand into small hollow spheres.
Unilever

considered when a soap powder is manufactured. Therefore ingredients are put in which help to soften the water or preserve the washing machine from chemical attack or help to make the powder attractive and pourable. All these ingredients are mixed in with the soap, and the hot mix is sprayed under high pressure through nozzles into a cooling tower. The droplets solidify as they fall and cool, and they are caught as granules on a conveyor belt at the base. This technique is known as 'spray-cooling'. Things such as chemical bleach, fluorescent dyes, and perfume, all of which would decompose if put into the hot mix, are finally added and the product is fed to a packeting machine.

Making non-soapy detergents – Non-soapy detergent powders are made to look as much as possible like soap-powders. They are manufactured so that they can do the same work.

To make a detergent powder, a hot mix of ingredients is sprayed through a high-pressure nozzle into a tower, and descends as droplets through an upward current of hot air. As the water in the droplets evaporates, so the droplets expand into hollow spheres. This technique is called 'spray-drying'.

Because of technical difficulties in the processing, solid tablets of non-soapy detergents have yet to compete with conventional bars of soap. However, non-soapy detergents are produced in concentrated liquid solutions, and these are extensively used for washing-up. Apart from nonionics, which are usually liquid to start with, the main difficulty in producing these liquid detergents is that the product contains a number of constituents which will go separately into concentrated solution, but, mixed together, throw one another out of the solution. The answer is to include another substance which has an affinity for all the incompatible constituents and

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which induces them all to stay in solution or in stable suspension. Such a substance is called a *solubilizer*.

The market for non-soapy detergents – Non-soapy detergents were introduced into Germany and the United States in the 1930s but it was not until during the Second World War, when fats were in short supply, that they came into use in this country. Nowadays the consumption of these detergents far exceeds that of soap, and there is every prospect that their consumption will increase.

Simplified flow chart showing stages in the manufacture of an alkyl-aryl sulphonate detergent.
Unilever
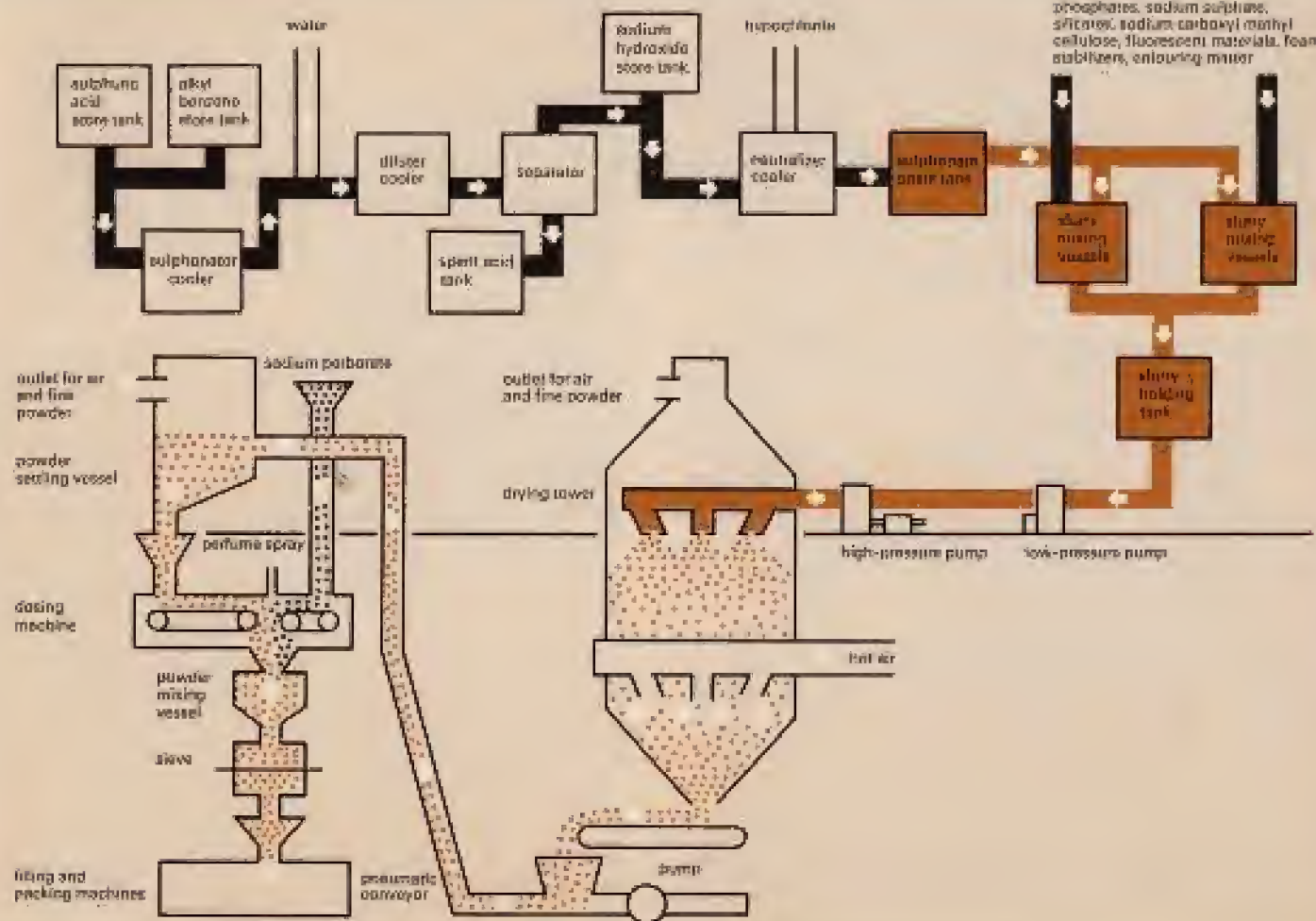
1. What properties are required of a detergent?

2. The hydrocarbon chain in a non-soapy detergent molecule usually contains about twelve carbon atoms. What would be the effect of (a) shortening the chain? (b) lengthening the chain?

3. How would you expect soap molecules to behave in a liquid such as kerosine?

4. Is soap a cationic, anionic or nonionic detergent? Apart from considerations of price and absence of scum, why is it desirable that detergents should be made from substances other than fats?

Some of the most useful non-soapy detergents are liquids for washing-up. Here dish-washing tests are being carried out to evaluate the performance of different products. *Shell*